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CITATION:

WADA, Tatsuhiko. On the physical properties within the B-layer deduced from olivine-model and on the possibility of polymorphic transition from olivine to spinel at the 20° Discontinuity. Bulletins - Disaster Prevention Research Institute, Kyoto ...

ISSUE DATE:

1960-08-30

URL:

<http://hdl.handle.net/2433/123695>

RIGHT:

DISASTER PREVENTION RESEARCH INSTITUTE

BULLETIN No. 37

AUGUST, 1960

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AT THE 20° DISCONTINUITY

BY

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ABSTRACT

An equation of state of forsterite is deduced theoretically based upon ionic model. The calculated variations of the density and incompressibility with pressure agree with those obtained by Bullen for the B-layer. Moreover, the activation energy of forsterite having Schottky defects is evaluated to be 3.29 *e.v.*, which is compatible with the experimental value of 3.0 *e.v.* measured by Hughes. The variation of the activation energy with pressure is investigated, and it is resulted that the extrapolation from the experimental values obtained within 10,000 *bars* is not reliable and the second derivative of activation energy concerned with pressure is not meaningless. The temperature distribution thus obtained within the B-layer is well in accordance with Gutenberg's one. By comparing the lattice energies of olivine and spinel (normal and inverse), which is evaluated theoretically, we find that the polymorphic transition from olivine to spinel is impossible.

1. Introduction

The opinion that the B-layer is composed of dunite is supported widely with geophysical, geochemical and petrological evidences. But many problems are yet open to discussion, for example, to investigate whether the variations of physical properties of dunite with pressure agree or not with those within the B-layer, is one of these problems.

We have only two observed quantities on the physical states of materials

composing the earth's interior: the distributions of seismic wave velocities and electric conductivities. Dunite is expected to have the physical properties deduced from those geophysical data.

Olivine, main constituent of dunite, contains usually 90 per cent forsterite (Mg_2SiO_4) and 10 per cent fayalite (Fe_2SiO_4). Thereupon the physical properties of forsterite should play most weighty part in those of the B-layer. We will estimate the physical properties of forsterite based upon solid-state physics, especially from microscopic point of view, since this kind of investigation for minerals has been little developed due to difficulties arising from complicated structure of minerals.

Another problem of olivine-model for the B-layer is concerned with the origin of the C-layer, which has peculiar physical properties. They are an abnormal increase of seismic wave-velocities and an abrupt anomaly of electric conductivity. Such an extraordinary behavior of the C-layer yields an attraction of many geophysicists and enormous numbers of papers have been published on the origin of the C-layer. At present the following two types of hypothesis are current: a polymorphic phase-transition hypothesis which is realized by a change in physical states of silicate, and a chemical transition hypothesis which is realized by a chemical inhomogeneity there. We will discuss in this paper a possibility of polymorphic transition of forsterite from olivine-structure to spinel structure.

2. An equation of state of forsterite and its elastic properties

According to Bragg's result (1937), Mg_2SiO_4 crystal is orthorhombic and has the three axes of the following length:

$$a = 4.755 \text{ \AA} \quad b = 10.21 \text{ \AA} \quad c = 5.985 \text{ \AA}.$$

In Fig.1 the structure of Mg_2SiO_4 (olivine-structure) is shown. The cohesive property of Mg_2SiO_4 seems to be of both ionic and covalent, and hence is considerably complicated. As the first approximation, the assumption that Mg_2SiO_4 is an ionic crystal containing Mg^{2+} , Si^{4+} and O^{2-} may be acceptable, although the exact evaluation needs quantum mechanical treatment. As an expression for lattice energy of ionic crystal, Born and Mayer (1932) gave the following,

$$u(v) = -A/(v/v_0)^{1/3} + B \exp\{-(v/v_0)^{1/3}/\rho\}, \quad (1)$$

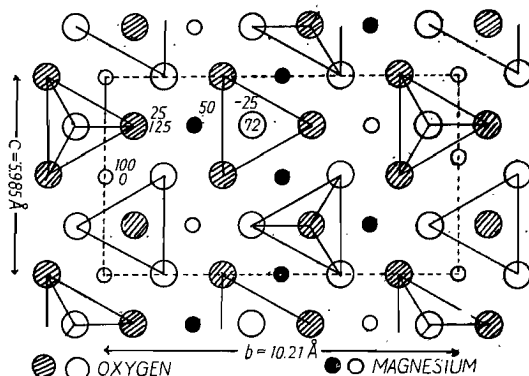


Fig. 1. Olivine structure of Mg_2SiO_4 . Si atom of which position is the center of O-tetrahedral, is not shown in the figure.

where v shows volume per molecule, and A, B and ρ are constants but depend upon the crystal structure and the constituent ions, and the suffix 0 refers to zero pressure. We should prefer the expression (1) to another expression

$$u(v) = -A/(v/v_0)^{1/3} + B/(v/v_0)^{n/3}$$

which are also frequently used, since (1) has been shown by Pauling being able to be deduced from quantum theory, and our problem concerned with high pressure demands such a formula that is applicable to wide range of the variation of v/v_0 . The first term in (1) shows electrostatic potential energy, and A is called Madelung constant, as known for such simple crystals as NaCl, CsCl, rutile etc., but not for olivine structure. In the first place, we must evaluate the Madelung constant for olivine structure. This evaluation is carried out through summing up $e_i e_j / r_{ij}$ ($i \neq j$), where e_i is the charge of the i th-ion and r_{ij} the distance between the i th- and j th ions. Among several practical methods for this summing up, the method devised recently by Bertaut (1952) is most suitable to be applied for such a complicated crystal as olivine. This method is as follows: a spherically symmetric charge-distribution $\sigma(\vec{r})$ having the center at the center of each ion is replaced for the actual ionic charge, where \vec{r} is a vector showing the position from the center of the ion and, for convenience, we impose on $\sigma(\vec{r})$ the restriction that each $\sigma(\vec{r})$ may contact, but must not overlap each other, that is,

$$\sigma(\vec{r}) \dots \begin{cases} = C & |\vec{r}| \leq R \\ = 0 & |\vec{r}| > R \end{cases} \quad C = 3/4\pi R^3, \quad (2)$$

where we adopt a half of the minimum distance between Si^{4+} and O^{2-} as R of (2), which is the maximum value permitted without violating above restriction (2). Expanding the crystal charge density-distribution $\rho(\vec{r})$ deduced from these $\sigma(\vec{r})$ to a three-fold Fourier series, we obtain the potential φ satisfying Poisson's equation

$$\Delta\varphi = -4\pi\rho(\vec{r}). \quad (3)$$

The φ corresponds to the first term of (1), namely the electrostatic potential energy. In practical calculation, we adopt the center of Mg^{2+} as origin and rectangular coordinates parallel to the three axes of olivine crystal lattice and then summation is over all ions within the sphere having the sufficient radius to contain the twelfth cell (the unit cell is composed of 8Mg^{2+} , 4Si^{4+} and 16O^{2-}) along a -axes from the cell containing the origin. Then we obtain

$$Ae^2/(\nu/\nu_0)^{1/3} = 155.22e^2/b \quad (4)$$

for a molecule, where b is the length of b -axes.

The second term of (1), expressing the repulsive potential energy due to the overlapping between each electron-cloud, has two unknown parameters B and ρ . To determine these, we differentiate (1) with ν once and twice, and then the expressions for pressure p and incompressibility K ,

$$p = -du(\nu)/d\nu = (1/3\nu) \left[-A/(\nu/\nu_0)^{1/3} + B\{(\nu/\nu_0)^{1/3}/\rho\} \exp\{-(\nu/\nu_0)^{1/3}/\rho\} \right] \quad (5)$$

$$K = -\nu dp/d\nu = (1/9\nu) \left[-A/(\nu/\nu_0)^{1/3} + B\{(\nu/\nu_0)^{1/3}/\rho\} \exp\{-(\nu/\nu_0)^{1/3}/\rho\} + B\{(\nu/\nu_0)^{2/3}/\rho^2\} \exp\{-(\nu/\nu_0)^{1/3}/\rho\} \right] + p, \quad (6)$$

are obtained. For static equilibrium $p=0$, using the experimental value for the incompressibility K of Mg_2SiO_4 at zero pressure, we can determine B and ρ . The explicit expression of (1) thus obtained is as follows :

$$u(\nu) = 350.709185/(\nu/\nu_0)^{1/3} + 5890.089736 \exp\{-4.2735(\nu/\nu_0)^{1/3}\}. \quad (7)$$

From (5), (6) and (7), the variations of K , and the density d with $(\nu/\nu_0)^{1/3}$ are evaluated, where for $(\nu/\nu_0)^{1/3}=1$, $d=3.3 \text{ gr/cm}^3$ is adopted (the calculation by using atomic weights and lattice dimensions gives 3.216 gr/cm^3). These results are shown in Table 1. Comparing these values with those

obtained by Bullen (1943) for the *B*-layer, we can find well accordance between both values (see Fig. 2). In fact, both values of d agree perfectly and even the maximum discrepancy between both of K amounts to only 8 per cent, which may be found to correspond to difference in the seismic velocities for a given depth of as much as 2 or 3 per cent, as pointed out by Birch (1939), since uncertainty in K/d is increased several times due to the fact that K/d is deduced from $V_p^2 - (3/4)V_s^2$ (V_p and V_s are the velocities of compressional and shearing waves, respectively). In addition, considering that the calculated value denotes isothermal one and the "observed value" adiabatic, the discrepancy as above cited should be regarded as a slight one.

Table 1. Variation of density d , incompressibility k and pressure p of Mg_2SiO_4 versus change $(v/v_0)^{1/3}$.

$(v/v_0)^{1/3}$	p (10^{12} dynes/cm 2)	k (10^{12} dynes/cm 2)	d (gr/cm 3)
1	0	1.22	3.30
0.99	0.039	1.32	3.40
0.98	0.082	1.44	3.51
0.97	0.129	1.56	3.62
0.96	0.180	1.70	3.73

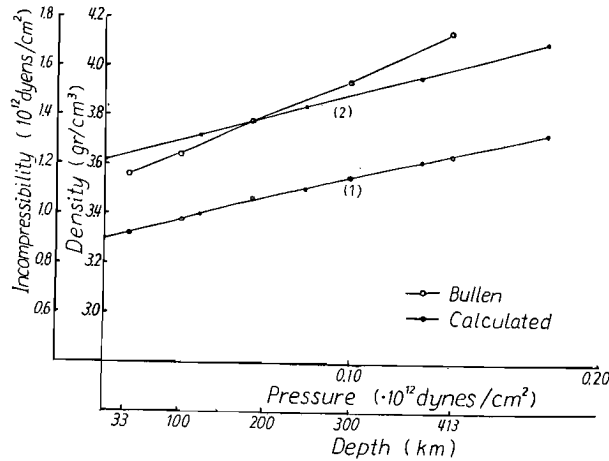


Fig. 2. Distribution of density (curve 1) and incompressibility (curve 2) within the *B*-layer.

3. Electric conductivity of Mg_2SiO_4

The electric conductivity of material within the Earth is deduced from geomagnetic data. On the other hand, Coster (1948) found that the electric conductivity σ of igneous rock is expressed by

$$\sigma = \sigma_0 \exp(-E_A/kT) \quad (8)$$

where E_A is called activation energy, k is Boltzman's constant and σ_0 is constant. This result means that the electric conductivity of igneous rock increases with temperature in a similar way to that of ionic and semi-conductors. Coster, Hughes (1955) and Rikitake (1952) estimated the temperature within the Earth from formula (8) in connection with the distribution of the electric conductivities "observed" within the Earth. However, their treatments of the variation of E_A with pressure come into question, for example, Coster's treatment is restricted to the variation of the thermal-vibrational term of E_A , and Rikitake's contains an uncertainty in the estimation of the pressure-dependence of lattice energy and, in addition, disregards the variation of polarization energy with pressure (the details will be cited later: also see T. Wada, (1958)). At any rate, this problem is desired to be studied further.

Hughes has shown that olivine exhibits three types of conduction. Above $1,000^\circ\text{C}$ the conduction becomes primarily ionic (see Runcorn and Tozer, (1955)). In present section, we may consider only ionic type of conduction, since ionic type prevails the other types within the B -layer, where the temperature is anticipated above $1,000^\circ\text{C}$. Ionic conductors are insulators in which certain mobile ions may move through the crystal lattice as result of defects in it. Assuming a Schottky defect, for Mg_2SiO_4 (in most of ionic crystals Schottky type is more advantageous than Frenkel type) (see Mott and Gurney (1948)), the activation energy E is represented with

$$E_A = (1/2)(W_L + W_+ + W_-) + U \quad (9)$$

where W_+ is the work required to remove a positive ion out of crystal, W_- the work required to remove negative ion, W_L the lattice energy of the crystal per ion-pair, and U is the work required to move the ion or hole half way to its next metastable position. We may consider Mg^{2+} and O^{2-} as the mobile ions, since Si^{4+} , having higher charge than Mg^{2+} , requires

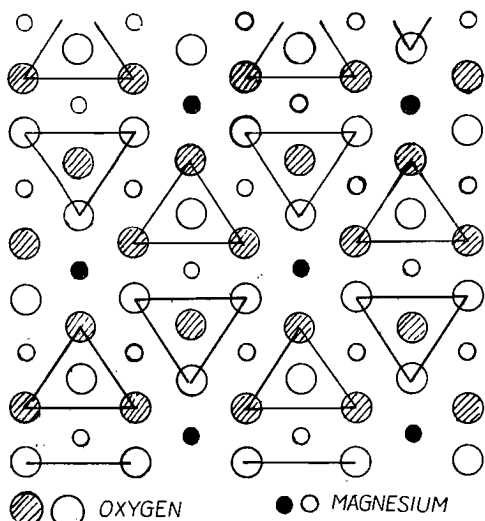


Fig. 3. Spinel structure of Mg_2SiO_4 , of which a section most similar to Fig. 1 is shown.

higher energy to be removed than Mg^{2+} .

(a) We can not directly estimate W_L , since the lattice energy of olivine obtained in the previous section can not be shared to the three kinds of ions. Fortunately, the electrostatic potential energy of spinel structure, which is very similar to olivine structure (Fig. 3 and Fig. 6; see also section 4), has been evaluated by Verway, de Boer and van Santen (1948), whose result carried out with Ewald's method

is separable for the three kinds of ions. Thereupon we assume that $l_{0a}/L_0 = l_{sa}/L_s$, where

L_0 : lattice energy of olivine structure per molecule

L_s : electrostatic energy of spinel structure per molecule

l_{0a} : lattice energy per a -ion in olivine structure

l_{sa} : electrostatic energy per a -ion in spinel structure.

($a = Mg^{2+}$, Si^{4+} and O^{2-})

Finally we get

$$W_L = 35.84 \text{ e.v.}, \quad (10)$$

from above assumption and (7).

(b) W_+ and W_- are calculated through the method devised by Mott and Littleton (1937). When an ion is removed, the medium surrounding the vacant lattice point will find itself in an electric field. It therefore becomes polarized, and in calculating W_+ or W_- the energy of this polarization must be taken into account. The polarization of the surrounding medium will set up at the vacant lattice point an electrostatic potential, which we denote by ϕ_+ or ϕ_- . Then the work necessary to remove an ion will be, instead of W_L ,

$$W_+ = W_L - (1/2)Z_+e\phi_+ \quad \text{or} \quad W_- = W_L - (1/2)Z_-e\phi_-. \quad (11)$$

Our problem is to calculate ϕ_+ and ϕ_- . We discuss first the problem of a rigid lattice, in which the ions are not allowed to move away from their mean positions, but in which they have polarizabilities

$$a_{Mg}=0.094, \quad a_{Si}=0.0165 \quad \text{and} \quad \alpha=2.4. \quad (10^{-24} \text{ cm}^3)$$

Suppose a charge e is placed at a definite point of the lattice, referred to as the point Q. Then dipoles are induced on all other ions. If r is the distance from Q, the center of the hole, we have for the polarization P

$$P=(1/4\pi)\{1-(1/\epsilon_0)\} (e/r^2) \quad (12)$$

where ϵ_0 is the dielectric constant for alternating fields, that is obtained from the polarizabilities of ions in connection with Clausius-Mossotti's formula. The dipoles on the three kinds of ions are respectively

$$\mu_i = \{a_i / (2a_{Mg} + 4a_0 + a_{Si})\} (1/4\pi) (1 - (1/\epsilon_0)) (ve/2r^2) \quad (13)$$

($i = \text{Mg, Si and } 0$)

where v is volume per an ion-pair of Mg^{2+} and O^{2-} . Since a dipole μ_i at a given lattice point gives a potential μ_i/r^2 at Q, we obtain the potential by summation:

$$\phi = \sum_{Mg} \mu_{Mg}/r^2 + \sum_{Si} \mu_{Si}/r^2 + \sum_0 \mu_0/r^2, \quad (14)$$

where the summations are over the lattice points of type Mg, Si and 0. Summations of these type have carried out with Misra's method. We pass on to the case of an actual crystal in equilibrium in a static field, so that the ions are displaced into new positions. Let $-cx$ be the restoring force, due to overlap forces, on any ion in a uniformly polarized medium where each ion is displaced by a distance $\pm x$. Then dipoles $\bar{\mu}_i$ induced at the lattice points of types Mg^{2+} , Si^{4+} and O^{2-} are

$$\bar{\mu}_i = a_i \{E + (4\pi/3)(P_0 + P_1) + (Z_i e/2c)^2\} \{E + (4\pi/3)(P_0 + P_1)\} \quad (15)$$

($i = \text{Mg, Si and } 0$)

where E is the electric field due to absence of ion, that is, $E = Ze/\epsilon r^2$, ϵ is the dielectric constant for static field, P_0 is the polarization due to the induced dipoles on the ions and P_1 is the polarization due to the displacement of the ions. E , ϵ , P_0 and P_1 is deduced from a_i and c . To obtain directly the c for Mg_2SiO_4 is very difficult. But we can find the c for MgO , which contains Mg^{2+} and O^{2-} and has similar elastic properties to Mg_2SiO_4 . (According to Szigetti (1950), we must consider the difference

between the c deduced from the experiment of elasticity and the c calculated from the dispersion frequency.) From these values and (13), we get

$$(1/2)Z_+e\bar{\phi}_+ = 18.63 \text{ e.v.}, \text{ and } (1/2)Z_-e\bar{\phi}_- = 12.36 \text{ e.v.},$$

where the $\bar{\phi}_+$ and $\bar{\phi}_-$ are the potentials in the case of a deformable lattice corresponding to the ϕ_+ and ϕ_- in the case of a rigid lattice.

(c) U in (9) is interpreted by Koch and Wagner as the activation energy of "structure-sensitive" ionic conduction, that is due to a trace of impurity in the crystal, acting in a way similar to the Cd ions in the silver salts. According to Hughes' experiment, the conduction of olivine under low temperature ($<600^\circ\text{C}$) is of "impurity" type, the activation energy of that is 1 e.v., compatible with those of common "structure sensitive" conductions. Moreover, the value of σ_0 , $10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$, is acceptable in the case of "structure sensitive" conduction. The assumption that 1 e.v. is adopted as U may be reasonable.

From (a), (b) and (c), the activation energy E_A becomes

$$E_A = 3.29 \text{ e.v.},$$

which agrees well with the experimental value of olivine, 3.0 e.v..

By estimating the variations of W_L , W_+ , W_- and U with pressure, we can find the variation of the activation energy E_A of Mg_2SiO_4 with pressure. (i) The variation of W_L is easily estimated, since this follows that of the lattice energy, given in section 2. (ii) The variation of W_+ and W_- can not be exactly expressed, since a_i and c also depend on pressure in unknown connection. We consider three cases of the variation of W_+ or W_- with pressure: (case 1) independent of pressure, (case 2) varies with $v^{-1/6}$ and (case 3) varies with $v^{-1/8}$. (iii) The variation of U also can not be exactly estimated, since we cannot find the repulsive potential in the neighbourhood of the center of ion. We assume that U varies with $v^{-12/3}$. (iv) temperature also affects E_A , since ionic conduction predominates above $1,000^\circ\text{C}$. The influence of temperature upon E_A is estimated by using the equation of state of Mie-Grüneisen:

$$p + du(v)/dv = \gamma E_{vib}/v, \quad (16)$$

where γ is Grüneisen constat, $\gamma = 1.2$ for Mg_2SiO_4 , and E_{vib} is as follows:

$$E_{vib} = (9/8)\Theta \cdot k + 3k \cdot T \cdot D(\Theta/T), \quad (17)$$

which shows the vibration-term of the lattice energy, where Θ is Debye tem-

perature, and $D(\bar{H}/T)$ is Debye function. The variation of \bar{H} with pressure is given by $\bar{H} = \bar{H}_0(v/v_0)^{-\gamma}$ ($\bar{H}_0 = 726^\circ K$ for Mg_2SiO_4). The temperature effect thus estimated is shown in Fig. 4, where we find, at $T = 500, 1,000$ and $1,500^\circ K$, the thermal expansions of Mg_2SiO_4 are 0.3, 0.6 and 1.0 per cent, corresponding to decreases of pressure of 3,000, 6,900 and 10,300 bars, respectively.

From (i), (ii), (iii) and (iv), in the case of $T = 1,500^\circ K$, the variation of E_A with pressure is evaluated. The results are shown

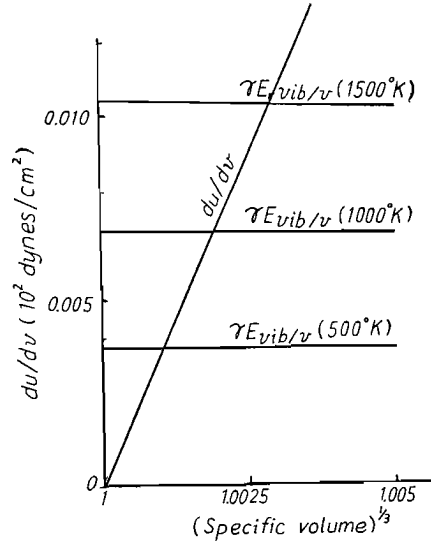


Fig. 4. Graphical solution of the equation of state of Mie-Grüneisen.

Table 2. Pressure dependence of activation energy at $1500^\circ K$.

p (10^{12} dynes/cm 2)	E_A (e.v.)		
	(case 1)	(case 2)	(case 3)
0	3.250	3.265	3.296
0.010	3.290	3.290	3.290
0.019	3.405	3.370	3.260
0.092	3.515	3.420	3.210
0.137	3.620	3.480	3.150
0.187	3.720	3.570	3.100

(case 1) $(1/2)Z_{Mg}e\bar{\phi}_{Hg} + (1/2)Z_0e\bar{\phi}_0 = \text{const}$
 (case 2) $\propto (v)^{-1/6}$
 (case 3) $\propto (v)^{-1/3}$

in Table 2., from which we can find the following: d^3E/dR^2 (R denotes the distance from the center of the Earth) is not zero, as mentioned by Verhogen (1956), even in the B-layer. In fact, $dE_A/dp = 4.0 \cdot 10^{-6}$ e.v./bar at $p = 0 \sim 10,000$ bars, and $dE_A/dp = 2.0 \cdot 10^{-6}$ e.v./bar at about 150,000 bars.

Therefore, the extrapolation of dE_A/dp derived by any experiment under low pressure ($p < 10,000$ bars) will result in overestimating the temperature within the Earth's interior, as mentioned by Hughes.

Considering the Hughes's value of $dE_A/dp = 4.3 \cdot 10^{-8}$ e.v./bar for peridot, we should take (case 1). When we adopt $10 \text{ ohm}^{-1} \text{ cm}^{-1}$ as σ_0 and the d -curve given by Lahiri and Price (1939) (1) and the distribution given by Rikitake (1950, 1951) (2) are adopted as the distribution of the electric conductivities within the B-layer, the temperature distribution, is obtained, as given in Table 3 and shown in Fig. 4. For comparison, the temperature

Table 3. Temperature distribution within the B-layer.

depth (km)	Temperature °K	
	(1)	(2)
100	1,820	1,500
200	1,920	1,540
300	2,010	1,580
400	2,100	1,600
Mean of dT/dR	$1^\circ/\text{km}$	$0.4^\circ/\text{km}$

- (1) calculate d value based upon Lahiri and Price's d -curve.
 (2) calculated value based upon Rikitake's model.

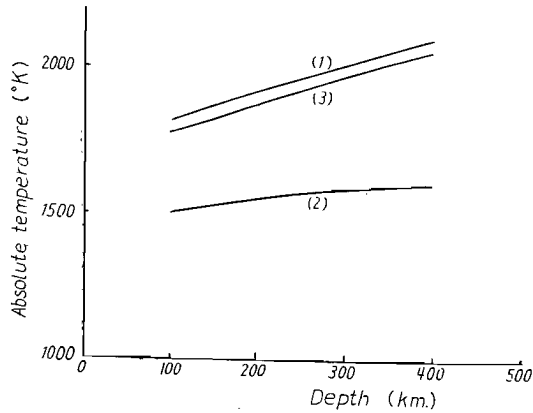


Fig. 5. Temperature distribution within the B-layer.

- (1) calculated value based upon Lahiri and Price's d -curve.
 (2) calculated value based upon Rikitake's model.
 (3) Gutenberg's result.

distribution given by Gutenberg is also shown in Fig. 4.

4. Possibility of the polymorphic transition of Mg_2SiO_4

Bernal suggested first the possibility of polymorphic transition of olivine at meeting when Jeffreys reported the existence of the *C*-layer. The magnesium germanate (Mg_2GeO_4) has a similar chemical formula to Mg_2SiO_4 and shows a polymorphic transition. Thus he inferred that the same kind of polymorphic transition might take place for Mg_2SiO_4 . Goldschmidt reported that Mg_2GeO_4 has two types of possible crystal structures, viz. olivine type (orthorhombic) and spinel type (cubic). Many other experimental works have been carried out to confirm the above report. Romeijn and Ringwood found that Mg_2GeO_4 changes its structure from spinel to olivine at about 600°C . On the other hand, Bridgeman found by high pressure experiments that the olivine shows a discontinuous jump of shearing strength at 84 *kbars*. He suggested that this discontinuous jump may be related to its polymorphic transition of crystal structure.

A theoretical study of the polymorphic transition of crystal has been carried out on ionic crystals, especially on a simple crystal such as alkali halides. One way of attack is to calculate the lattice energy based upon a classical treatments. Though the results thus obtained give transition-pressures, the values are so unreliable that only the possibilities of transitions are confirmed, even if higher terms of energies are considered and the dependence on pressure is estimated as exactly as possible. (see, for instance, Jacobs (1938), and Born and Hung (1954)).

A stability condition of crystal at high pressure and at absolute zero temperature is given by examining the Gibbs free energy (or enthalpy) $U+PV$. U , P and V denote lattice energy, pressure and volume. When the transition takes place at the pressure P , the stability condition gives

$$U_A + PV_A = U_B + PV_B \quad (18)$$

or

$$P = (U_B - U_A) / (V_A - V_B) \quad (19)$$

Neglecting the effect of pressure upon U and V for the first approximation (as above mentioned, we should be concerned with the possibility of transition only), we get

$$P \cong (U_{B,0} - U_{A,0}) / (V_{A,0} - V_{B,0}) \quad (19')$$

where the suffix 0 denotes the value at $P=0$.

The repulsive energy represented by exponential type in (1) is a rigorous expression. However the inverse power type is frequently used for many practical problem owing to its simple expression. In the following we use the lattice energy as

$$U = -(A/r) + (B/r^n) \quad (20)$$

From the equilibrium condition $(dU/dr)=0$, the value r_0 and U_0 at $P=0$ are given by

$$r_0 = (nB/A)^{1/(n-1)}, \quad U_0 = -(A/r_0) / \{(n-1)/n\} \quad (21)$$

From (19') and (21), we get

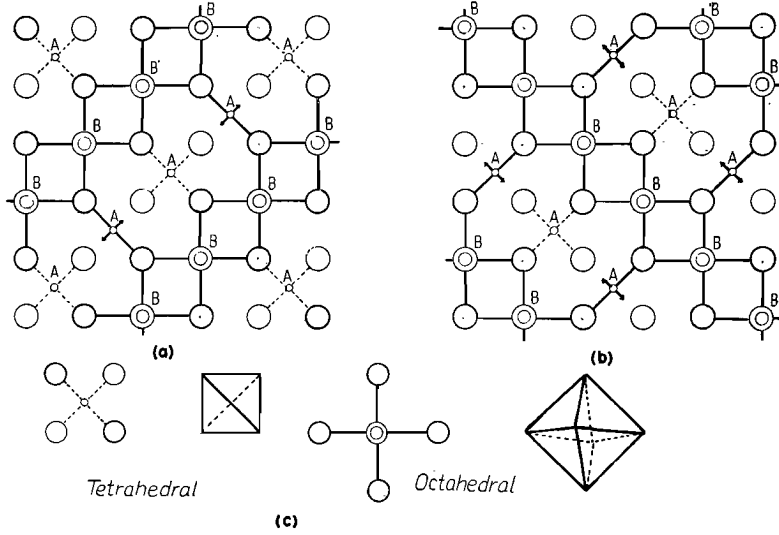


Fig. 6. The structure of spinel.

The structure in idealized form. The oxygen atoms (shown by large circles) are approximately in cubic closed packing. (a) and (b) show two close-packed layers projected upon the cubic face. One set of silicon atoms (shown by small circles A) is in positions of four-coordination between a tetrahedral group of oxygen atoms and the other set of magnesium atoms (shown by small circles B) in six coordination between an octahedral group. (shown in (c)) We may picture as a series of layers as above shown. The bottom layer of (a) has diagonal chains of magnesium-octahedra, which are linked laterally by silicon-tetrahedra lying alternately above and below heavily outlined oxygen atoms. In the next layer (b), the slant of the chains is reversed. Four such layers makes up the complete unit cell.

$$P = (A/sr_0^4)F_n \quad (22)$$

$$F_n = \{ (n-1)/n \} \{ 1 - (A_B/A_A)^{n/2(n-1)} (B_A/B_B) \} / \{ 1 - (s_B/s_A) (B_B/B_A)^{3/2(n-1)} (A_A - A_B)^{3/2(n-1)} \}$$

where $V_A = s_A r_A^3$, $V_B = s_B r_B^3$.

The spinel XY_2O_4 has generally the spinel structure which is shown in Fig. 3 or Fig. 6 for the normal spinel structure. We notice that the Fig. 3 is quite similar to the olivine structure of XY_2O_4 shown in Fig. 1. In the normal spinel X-ions occupy the center of the O-tetrahedra (half of Y-ion in the inverse case). According to Verwey et al. the electrostatic potential energy of the spinel expressed by

$$U_{sp} = -(1/2)(e^2/a)(p M_{tetra} + 2q M_{oct} + 8M_0) = -M(e^2/a) \quad (24)$$

where

- a : length of the cube edge of the cubic lattice
- M_{tetra} : contribution from tetrahedral interstices
- M_{octa} : contribution from octahedral interstices
- M_0 : contribution from O lattice points
- p : ionic charge number of the tetrahedral interstices
- q : ionic charge number of the octahedral interstices

For the normal and inverse spinels $p=4$, $q=2$, and 2, $(1/2)(4+2)=3$, respectively. Table 4 is the numerical table for M . According to Bron and Mayer's expression, a repulsive potential R between two kinds of ions, α and β ,

Table 4. Electrostatic energy of normal and inverse spinel for several values of oxygen parameter (unit : $(e^2/a) 10^{-12} \text{ erg}$) (after Verwey et al.)

Parameter u	Charge $p \ q$	M_{tetra}	M_{oct}	M_0	M
0.375	4 2	24.94	15.00	14.55	138.1
	2 3	17.53	17.99	14.27	138.6
0.380	4 2	23.63	16.23	14.00	135.8
	2 3	16.25	19.23	14.35	131.4
0.385	4 2	22.50	17.47	13.42	133.6
	2 3	15.10	20.47	14.37	134.0
0.390	4 2	21.41	18.71	12.82	131.5
	2 3	14.01	21.70	14.35	136.5

(For explanation see (24))

$$R = C\lambda_{a,\beta}\bar{b}\exp\{(r_a + r_\beta - r_{a,\beta})/\rho\} \quad (25)$$

where C and \bar{b} are the coordination number and a constant, respectively, and $\lambda_{a,\beta}$ is expressed by

$$\lambda_{a,\beta} = 1 + Z_a/N_a + Z_\beta/N_\beta \quad (26)$$

where Z is the charge of ion, N is the number of electron in the outer-shell of ion, and the suffix α or β denotes α - or β -ion, r_a , r_β and $r_{a,\beta}$ in (25) are basic radii of α - and β -ions and the nearest distance between both ions, respectively. Referring to (25) and (26) we obtain the repulsive potential R per molecule as follows:

for olivine-structure

$$\begin{aligned} R_{oe} = & 4\lambda_{st,0}\bar{b}\exp\{(r_{st} + r_0 - 0.1777b)/\rho\} \\ & + 12\lambda_{mg,0}\bar{b}\exp\{(r_{mg} + r_0 - 0.2044b)/\rho\}, \end{aligned} \quad (27)$$

for normal spinel-structure,

$$\begin{aligned} R_{ns} = & 4\lambda_{st,0}\bar{b}\exp\{(r_{st} + r_0 - \sqrt{3}a/8)/\rho\} \\ & + 12\lambda_{mg,0}\bar{b}\exp\{(r_{mg} + r_0 - a/4)/\rho\}, \end{aligned} \quad (28)$$

and for inverse spinel-structure,

$$\begin{aligned} R_{is} = & 4\lambda_{mg,0}\bar{b}\exp\{(r_{mg} + r_0 - \sqrt{3}a/8)/\rho\} + 6\lambda_{mg,0}\bar{b}\exp\{(r_{mg} + r_0 - a/4)/\rho\} \\ & + 6\lambda_{st,0}\bar{b}\exp\{(r_{st} + r_0 - a/4)/\rho\}, \end{aligned} \quad (29)$$

where the constants ρ and \bar{b} are $0.345A$ and 10^{-12} erg , respectively.

To compare the energies of the three types of structures, viz. olivine, normal spinel and inverse spinel, it is convenient to transform the unit of length from a (cubic edge length of spinel) to b (b -axes length of olivine). By using this transformation, we set up approximately

$$\begin{aligned} & \exp(-0.1777b/\rho)/\exp(-0.2044b/\rho) \\ & \cong \exp(-0.1770b/\rho)/\exp(-0.20434b/\rho) \equiv G \end{aligned} \quad (30)$$

Then, referring to (22) and (30), B_A/B_B is expressed approximately by R_{oe} , R_{ns} and R_{is} .

We must consider the effect of oxygen parameter, as previously mentioned. It is well known that the actual spinel has u greater than 0.375. In the present section, the effect of oxygen parameter greater than $u=0.375$ is discussed. Putting $u=0.375+\delta$, then we replace $\sqrt{3}a/8$ and $a/4$ in (26) and (27) with $\sqrt{3}a\{(1/8)-\delta\}$ and $a\{(1/4)-\delta\}$, respectively.

In conclusion we have F_n and P in (23) as shown in Table 5, where $3 \leq n \leq 7$. The condition of transition from A to B is given by $F_n > 0$, and

Table 5. Signs of F_n and V_{ol}/V_{sp} for several values of n and u . The sufficient condition for a polymorphic transition is $F_n > 0$ and $V_{ol}/V_{sp} > 1$.

n	$u=0.375$		$u=3.80$	
	normal spinel	inverse spinel	normal spinel	inverse spinel
3	negative	negative	negative	negative
4	negative	positive < 1	negative	negative
5	negative	positive < 1	negative	negative
6	negative	positive < 1	negative	negative
7	negative	positive < 1	negative	negative

$V_A/V_B \geq 1$. In table 5 V_A/V_B is shown only for $F_n > 0$. The results thus obtained mean that the polymorphic transition from olivine to spinel (normal or inverse) is impossible.

5. Conclusion

The variations of the elastic and electrical properties of Mg_2SiO_4 with pressure agree well with those deduced from seismic data and geomagnetic data within the B-layer. It seems true that the B-layer is composed of dunite.

On the other hand, the possibility of polymorphic transition from olivine to spinel is denied at any rate. However to confirm the possibility of phase-transition theoretically, generally speaking, is a difficult problem, since whether the transisition is possible or not, depends upon the difference between the lattice energies of both phases. Even if the lattice energies of both phases is considerably well evaluated, the difference may be not reliable, though the unknown errors in both lattice energies are somewhat cancelled. Thereupon we should say that this problem is yet open to discussion.

Acknowledgements

The writer wishes to thank Prof. K. Sassa of the Geophysical Institute, Kyoto University, and Prof. H. Miki of Abuyama Seismological Institute, Kyoto University, for their continuous encouragements. The present study has been suggested by Dr. Y. Shimazu of the Institute of Earth Sciences,

Nagoya University, to whom the writer's thanks are due.

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Bulletin No. 37 Published August, 1960

昭和 35 年 8 月 25 日 印 刷

昭和 35 年 8 月 30 日 発 行

編輯兼
発行者 京都大学防災研究所

印刷者 山 代 多 三 郎

京都市上京区寺之内通小川西入

印刷所 山代印刷株式会社